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Raman Spectra of Crystalline Inorganic Chlorides.

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(Plate VIII)

(*Received for publication, 22nd May, 1930.*)

ABSTRACT.

Numerous inorganic halides have now been examined in the form of crystalline powders using the same method as for the nitrates (*Nature*, March 22nd, 1930). Mercuric and mercurous chlorides showed remarkably intense and sharp lines. ($HgCl_2$, 312 cm^{-1} strong, 381 weak; Hg_2Cl_2, 167 and 275 strong, 295 and 320 weak). Linear models are postulated for the molecules of these two chlorides. The Raman spectrum of $HgCl_2$ shows a strong resemblance to that of CO_2 and of CS_2. A saturated solution of $HgCl_2$ in methyl alcohol showed a distinct broadening of the principal line (312 cm^{-1}).

Among the other chlorides, $ZnCl_2$ showed one faint line and CdI_2 three faint lines. A triangular model is indicated for these two substances. $SbCl_3$ and $BiCl_3$ each gave four sharp well-resolved lines shifted in position and much sharper than those recorded for liquid $SbCl_3$ and conc. solution of $BiCl_3$ by Daure. PCl_5 showed four Raman lines, but all the other chlorides examined, *viz.*, those of Li, NH_4, Mg, Ba, Cu (ic), Ag, Cd, Sn (ous) and Th as well as KI and PbI_2 did not show any lines, similar negative results having been recorded for NaCl, KCl, CaF_2 and NaF by Schaefer.

From the above observations the conclusion is arrived at, that covalent bonds are necessary for the production of the Raman effect, the magnitude of which could be determined directly from the known data on the conductivity of the molten chlorides, and less directly from crystal structure data, volatility, solubility and formation of volatile organic derivatives. Compounds where electrovalent linkages only are present fail to show the effect.

1. *Introduction.*

In a recent communication to Nature,[1] the present author has shown the possibility of photographing the complete Raman spectrum of substances in the form of coarse powders or crystalline aggregates. A large number of inorganic nitrates were examined in this way with satisfactory results.[2] This method has now been extended to a study of the inorganic halides, especially the chlorides, in view of the simplicity of their structure. There is, however, another unique interest attaching to this problem. Nearly every experimenter on the Raman effect has examined rock-salt for the rest-strahlen frequency recorded by the infra-red spectra, with decidedly negative results. Prof. Cl. Schaefer finds no lines even with various other cubic crystals,[3] *e.g.*, NaF, LiF, CaF_2 and KCl. On the other hand, the early work of Dr. P. Daure has shown that the chlorides of many non-metals, metalloids and a few metals, *viz.*, of C, Si, Ti, Sn, P, As, Sb and Bi show the Raman spectra in a marked manner.[4] The question naturally arises as to why the effect should appear very prominently in some cases, less so in some others and completely disappear in several other halides. The present investigation on several

[1] Nature, *125*, 463 (1930).
[2] Ind. J. Phys., *5*, 1 (1930).
[3] Schaefer, C. f. Phys., *54*, 153 (1929).
[4] Daure Compt. Rend., *187*, 940 (1928).

inorganic chlorides in the solid state was started with a view to provide a satisfactory explanation for these observed phenomena.

2. *Experimental Results.*

The same apparatus and procedure were employed as in the previous work on the inorganic nitrates. The mercury arc cooled by a slow current of air was placed close to the triangular cell containing the substance. The scattered light from the side of the cell was concentrated on the slit of the spectrograph by a system of lenses. A Fuess glass prism instrument of high dispersion was used, and exposures ranging from 1-2 hours on backed Ilford Isozenith plates were sufficient to bring out all the Raman lines. The following substances mostly of Kahlbaum and Merck were examined as such, *viz.*, chlorides of Li, Mg, NH_4, Ag, Au, Cu (ic), Ba, Zn, Cd, Hg (ous), Hg (ic), Sn (ous), Th, P, Sb, Bi ; also KI, $CdBr_2$, PbI_2 and CdI_2. Antimony and bismuth trichlorides and phosphorus pentachloride gave well-resolved lines. Exceptionally sharp and strong lines were observed with mercuric and mercurous chlorides, with intense anti-stokes components. With zinc chloride one faint line was observed, while with cadmium iodide and gold chloride (examined with 5461 green line of mercury) the Raman lines were feebler still. No lines were given by all the remaining halides. Table I summarises the results obtained with $HgCl_2$, Hg_2Cl_2, $ZnCl_2$, CdI_2,$SbCl_3$, $BiCl_3$ and PCl_5. An iron arc comparison spectrum was photographed on each plate, and the wavelengths calculated by linear interpolation from the nearest known iron lines.

TABLE I.

Raman Lines.

Substance.	Exciting line. λ in I. A.	Wave No.	Δν	λ in μ.	Intensity.
$HgCl_2$ (Mercuric chloride.	4358·34	(1) 22625·8	312·3	32·02	Strong.
		(2) 22556·9	381·2	26·23	Weak.
		23252	314	Anti-Stokes.	
Hg_2Cl_2 (Mercurous chloride).	4358·34	(1) 22771·4	166·7	60·0	Very strong.
		(2) 22663·5	274·6	36·42	Strong.
		(3) 22643·0	295·1	33·89	Weak.
		(4) 22618·1	320·0	31·25	Very weak.
		23102	164	Anti-Stokes	
		23208	270	,,	
$ZnCl_2$ (Zinc chloride.)	4358·34	(1) 22704·4	233·7	42·8	Weak.
CdI_2 (Cadmium Iodide).	5460·74	(1) 18202·3	105·2	95·1	,,
		(2) 17962·5	345·0	29·0	,,
		(3) 17912·3	395·2	25·3	,,
$SbCl_3$ (Antimony Trichloride).	4358·34	(1) 22792·3	145·8	68·6	,,
		(2) 22771·9	166·2	60·2	Medium.
		(3) 22626·1	312·0	32·05	,,
		(4) 22600·6	337·5	29·63	Strong.
$BiCl_3$ (Bismuth Trichloride).	4358·34	(1) 22785·1	153·0	65·4	Very weak.
		(2) 22769·0	169·1	59·1	Weak.
		(3) 22696·2	241·9	41·3	,,
		(4) 22649·9	288·2	34·7	,,
PCl_5 (Phosphorus Pentachloride).	5460·74	(1) 18059·6	247·9	40·3	,,
		(2) 17951·3	356·2	28·1	Medium.
		(3) 17902·7	404·8	24·7	Very weak.
		(4) 17857·9	449·6	22·2	Weak.

3. *Discussion of Results.*

Mercuric Chloride.—It can be seen from Table I that this substance gives rise to one very strong line with a faint companion on the long wavelength side (312 and 381 cm^{-1} respectively). The spectrum is quite analogous to that observed with liquid CS_2 as well as gaseous CO_2, both of which show two lines.[5,6] In the two latter substances, the Raman lines do not correspond to any of the known infra-red absorption bands, and hence are probably inactive frequencies analogous to the 9·5 μ frequency of the NO_3 ion in the nitrates. The absence of any permanent electric moment in CO_2 and CS_2 taken together with other evidence[7] strongly supports the linear symmetrical rod type of molecule for CO_2 suggested by Eucken.[8] The value for the inactive frequency calculated on this basis agrees very well with that of the observed Raman line. The essential similarity between the Raman spectra of CO_2, CS_2 and $HgCl_2$ strongly suggests a linear model for the $HgCl_2$ molecule, the Raman frequency $\Delta\nu = 312\ cm^{-1}$ representing the symmetrical vibration of the chlorine atoms towards and away from the central atom. (*cf.* $CO_2 = 1284$ and $CS_2 = 655\ cm^{-1}$).

We have still to explain the presence of the weak companion of the prominent Raman line. In $HgCl_2$, its value is $\Delta\nu = 381\ cm^{-1}$, in CS_2 it is 795 and in CO_2 1392 cm.$^{-1}$ It seems very probable that in all these cases we are dealing with a type of oscillation not contemplated by Eucken. It may arise from the oscillation of one of the chlorine atoms against the remaining group (Hg Cl) as a whole, the latter being supposed to be at rest. Similarly, the faint line in CS_2

[5] Petrikaln and Hochberg; Z. Phys. Chem., 3, 217 (1929).
[6] Rasetti, Nature, 123, 205 (1929).
[7] Rawlins, Trans. Farad. Soc., 25, 925 (1929).
[8] Eucken, Z. f. Phys., 37, 714 (1926).

and in CO_2 may be due to S—CS and O—CO oscillations respectively. As the occurrence of this type of oscillation is very limited, the corresponding Raman line is very feeble. It bears a certain analogy to "predissociation" of molecules [9] described by V. Henri, and is supported by chemical evidence. We know that at high temperatures as well as under the influence of light of short wavelength CO_2 breaks up into CO and O, CS_2 loses S and $Hg\ Cl_2$ is converted into $Hg_2\ Cl_2$. [10]

A very concentrated solution of mercuric chloride (about 40%) in methyl alcohol was also examined. The strong $HgCl_2$ line occurred practically in the same position as in the crystals, but a considerable broadening was quite evident. A similar broadening of the inactive frequency of the NO_3 ion was observed in the concentrated aqueous solution of lithium nitrate examined previously. [11] It seems probable that the symmetrical broadening observed in the solutions, and in some cases when passing from the solid to the liquid state is due to the increased rotational freedom of the molecules in the molten and dissolved states. These points will be discussed in detail in a separate paper to be published shortly.

Incidentally it may be pointed out that by analogy with CO_2, $HgCl_2$ also could be expected to possess a molecular lattice. The linear symmetrical model further indicates absence of any permanent electric moment, and hence the molecule should be non-polar.

Mercurous chloride (*calomel*).—The Raman spectrum of this substance consists of a very strong line (167 cm^{-1}) and a strong somewhat broad line (275) with two faint companions (295 and 320 cm^{-1}). It is obvious from the number of lines present that a simple formula like HgCl does not

[9] V. Henri, Nature, Dec. 20, 1924.

[10] Plotnikow, Kurzer Leitfaden der Photochemie (G. Thieme, 1928), pp. 48, 114 and 115.

[11] Krishnamurti Ind. J. Phys., *5*, 1 (1930).

correctly represent mercurous chloride. This is in harmony with chemical evidence and strongly supported by crystal structure data. The latter points to a molecular lattice of Hg_2Cl_2, the length of the molecule being parallel to the C—axis.[12] Hence a linear symmetrical model Cl-Hg-Hg-Cl is indicated for this substance, as for $HgCl_2$. The strong line (275 cm^{-1}) corresponds to the symmetrical movement of the chlorine atoms towards and away from the central Hg_2 group. The slower oscillation in this case as compared to $HgCl_2$ (312 cm^{-1}) can be explained as due to the greater heaviness of the central group (Hg_2). Its faint companion (295 cm^{-1}) corresponds probably to the Cl—Hg_2Cl oscillation. The origin of the still fainter line (320 cm^{-1}) cannot for the present be decided upon.

It should be remarked here that when mercurous chloride is exposed to the light of the mercury arc, the surface layer gets blackened on account of photochemical decomposition : $Hg_2Cl_2 \longrightarrow HgCl_2 + Hg$. The possibility of formation of sufficient $HgCl_2$ in the interior layers is however remote, and hence the faint line (320 cm^{-1}) may not be the $HgCl_2$ line (312 cm^{-1}), though the two frequency shifts lie very near together.

We have now to account for the very strong line ($\triangle\nu = 167$ cm^{-1}). Its strength indicates it as one of the inactive frequencies. The only possible way in agreement with the linear model postulated above for Hg_2Cl_2 is to assign it to the Cl Hg—HgCl oscillation.

On the basis of the above assumptions, if ν_1 represents the symmetrical oscillation of the chlorine atoms and ν_2 of the Hg atoms, a new combination frequency could be expected $\nu_1 - \nu_2$. This comes out as 108 cm^{-1} or 93 μ agreeing approximately with the rest-strahlen frequency for Hg_2Cl_2

[12] Hylleraas, Phys. Zeit., *26*, 811 (1925).

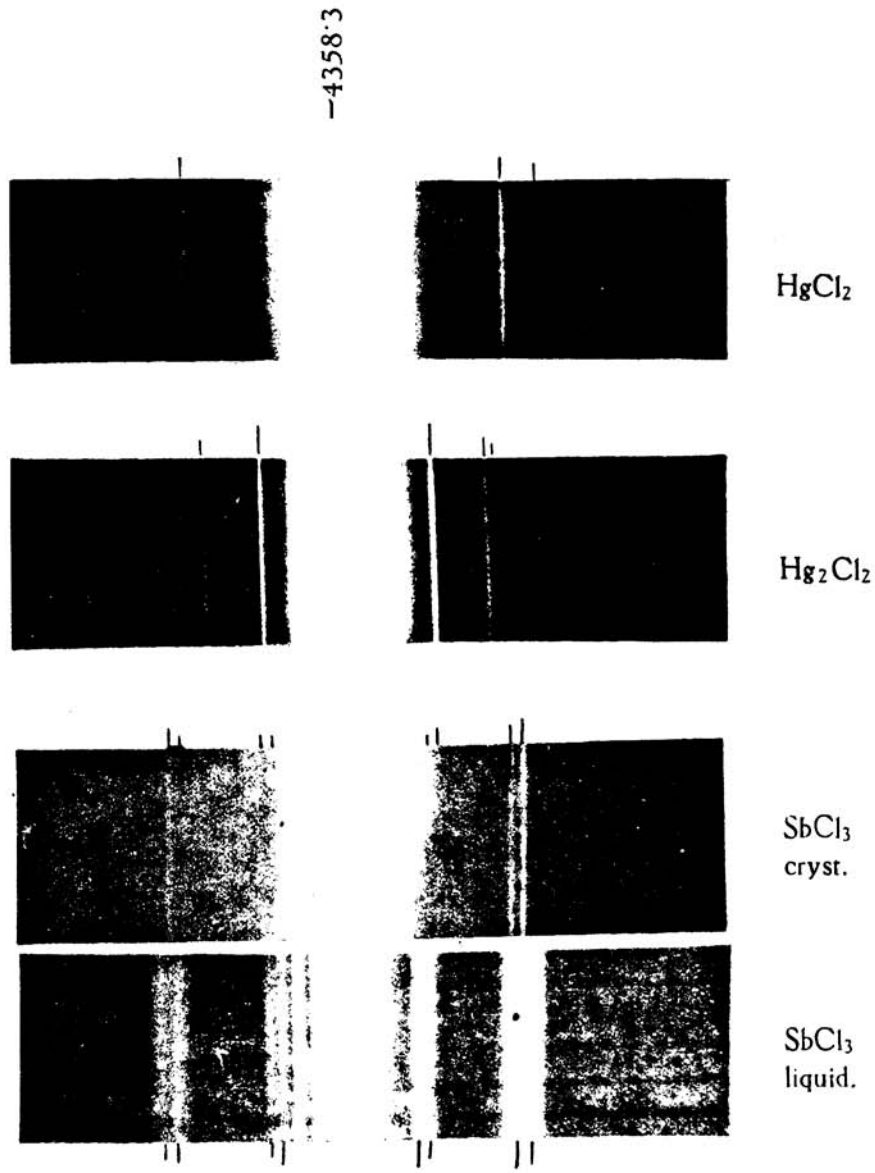
which is about 98μ. It is of course possible that this is only some chance coincidence since we usually regard the rest-strahlen frequency as a fundamental one.

Zinc chloride.—The anhydrous chloride was enclosed in an air-tight cell during the exposure. A single faint line (about 234 cm^{-1}) appeared, with indications of two more lines which, however, were rendered doubtful by the presence of diffraction lines consequent upon intense exposure of the incident lines. It is very likely that it is not the inactive frequency and hence an isosceles triangular model for this substance is indicated.

Cadmium iodide.—The substance investigated consisted of thin flakes. The surface layer got coloured during the exposure due to photochemical decomposition. Three Raman lines excited by the Hg green line 5461, all very weak, were observed. The Raman line (105 cm^{-1}) is probably the analogue of the $ZnCl_2$ line (234 cm^{-1}), the shift to shorter wavelengths in the former being due to the greater mass of I_2 as compared with Cl_2. The same isosceles triangular model will account for the three frequencies observed. This substance is interesting because no effect could be observed in the chloride and bromide. It further crystallises in the characteristic 'layer lattice' intermediate between the molecular and ionic lattices.

Antimony and Bismuth Trichlorides.—$SbCl_3$ has been examined in the liquid state (at about 100°C) by Daure[13] who found two doublets present. He has also examined $BiCl_3$ in a solution of conc. HCl. The relative intensities of the lines as well as their positions in the crystals differ very much from the values of Daure as the following table will show :

[13] Daure, *loc cit.*



Raman Spectra

TABLE II.

	$SbCl_3$.		$BiCl_3$.	
	Crystals $\Delta\nu$.	Liquid at 100°C (Daure).	Crystals $\Delta\nu$.	Conc. HCl Soln. (Daure).
(1)	146	130	153	110
(2)	166	155	169	—
(3)	312	320	242	240
(4)	338	360	288	290

It will be seen that with $SbCl_3$ crystals the first pair of lines has shifted towards longer wavelengths and the second pair to shorter. The same phenomenon could be noticed in $BiCl_3$ with the first pair of lines.* Further, the crystal lines are considerably sharper. The present author has considered the question of the change from the solid to the liquid state in the case of benzophenone.[14] A broadening of the line due to the ketonic group together with its shift towards longer wavelengths takes place on melting. Hence the polar bonds seem to be most influenced by the change of state, and this conclusion is confirmed by the results with antimony and bismuth chlorides which we know are polar. A fuller treatment of the change in state and how far it influences the Raman spectra of polar and non-polar compounds both organic and inorganic is reserved for a future communication.

Phosphorus Pentachloride.—This substance on account of its very reactive nature was examined in an air-tight container. Since it was coloured yellow and absorbed the blue

* This, however, is not certain since the lines were very faint and diffraction effects were present in that region.

[14] Krishnamurti, Nature, *loc. cit.*

line, the green mercury line was used as the exciting radiation. Four lines were found, but there were indications of a few more lines closer to the incident line. Until all the possible lines have been isolated it is difficult to picture any model for the PCl_5 molecule. It may, however be pointed out here that none of the lines conicide with those found for PCl_3 by Daure.

4. *Raman Effect and the Electronic Theory of Valency.*

It will be useful at this stage to classify the halides under three different groups :

(1) Those that show strong Raman lines, *viz.*, chlorides of Hg (ous) Hg (ic), P, As, Sb, C, Si, Ti, Sn and of hydrogen.

(2) Those that show faint Raman lines, *viz.*, $BiCl_3$ $ZnCl_2$, CdI_2 and $Aucl_3$.

(3) Those that show no lines at all, *viz.*, chlorides of Na, K, NH_4, Ba, Ag, Cu(ic), Cd, Mg, Sn(ous), Th as well as $CdBr_2$, PbI_2, KI, LiF, NaF and CaF_2. A consideration of the properties which the substances in any one group possess in common will enable us to understand the exact significance of the appearance or non-appearance of the Raman spectra.

Electrovalency and Covalency.—It will be seen from the above classification that the chlorides of the strongly electro positive elements do not show the effect while the chlorides of the non-metals and metalloids show it very well. A further distinction between the groups could be effected by finding out whether the union between any atom and chlorine is of the electrovalent (where electron transfer is complete) or covalent type[15] (where there is electron sharing). Since the former type of compounds are completely ionised while the latter are non-ionised, the obvious test for distinguishing between the two types is

[15] Sidgwick, Electronic Theory of Valency (Oxford, 1927).

by means of their conductivity. In the case of most of the inorganic chlorides, we have the data of Biltz and his co-workers on their conductivity just above their melting points.[16] The following table gives the specific conductivities of the various chlorides in reciprocal ohms at the specified temperature. They are arranged in the decreasing order of their conductivity :

TABLE III.

Chloride of.	Temp. in °C.	Eq. conductivity.	Chloride of.	Temp. in °C.	Eq. Conductivity.
Li	613	5·85	In^{III}	586	0·43
Ag	455	3·77	Bi^{III}	227	0·38
Na	800	3·54	Yt	700	0·37
Cu^{I}	422	3·25	U^{IV}	570	0·34
K	768	2·12	In^{II}	235	0·23
Ba	960	1·95	Te^{IV}	236	0·115
Ca	774	1·93	Te^{II}	206	0·042
Sr	873	1·90	Zn	318	8×10^{-4}
Cd	564	1·88	Hg^{II}	277	$0·8 \times 10^{-4}$
Rb	714	1·46	Mo^{V}	216	$1·8 \times 10^{-6}$
Pb^{II}	498	1·44	W^{VI}	280	$1·98 \times 10^{-6}$
La	860	1·12	As^{II}	0	$1·24 \times 10^{-6}$
Cs	645	1·11	Sb^{III}	73	$0·85 \times 10^{-6}$
Tl^{I}	430	1·09	Pb^{IV}	0	$0·8 \times 10^{-6}$
Mg	712	1·02	W^{V}	250	$0·67 \times 10^{-6}$
Pr	824	0·82	Al^{III}	194	$0·45 \times 10^{-6}$
Sn^{II}	245	0·78	Ta^{V}	230	$0·3 \times 10^{-6}$
Nd	775	0·63	Nb^{V}	220	$0·22 \times 10^{-6}$
Th	765	0·56	Se	18	$0·2-10^{-6}$
Sc	940	0·50			

[16] Gmelin's Handbuch der Anorg. Chem. (Verlag Chemie, Berlin, 1927).

In addition to the above, we have other chlorides enumerated below for which exact data are not available.

TABLE IV.

Good-conductors.	Non-conductors.	
$GaCl_3$	BCl_3	VCl_4
$CrCl_3$	CCl_4	$SbCl_5$
$InCl_3$	$SiCl_4$	S_2Cl_2
$MnCl_2$	$TiCl_4$	ICl
$FeCl_3$	$GeCl_4$	ICl_3
$CoCl_2$	$SnCl_4$	
$NiCl_2$	PCl_3	
$PdCl_2$	PCl_5	

It will be seen from tables III and IV that only non-conductors and very feeble conductors show the Raman effect while good conductors do not show the effect at all. We know also that gaseous [17] and liquid HCl [18] which are non-conductors show the effect which however disappears once it is dissolved in water where it ionises and becomes an excellent conductor. The case of mercuric chloride is indeed very striking. The conductivity of the molten substance is very low and even in aqueous solutions it is but very little ionised. In fact as Sidgwick remarks, [19] "the tendency of mercury to assume the convalent form is quite exceptional, and must be due in part to causes outside the Fajans theory." We also find that the Raman spectra of the mercury chlorides are surprisingly

[17] Nature, *123*, 279 (1929).
[18] Salant and Sandow, Phys. Rev., *33*, 1096 (1929).
[19] Sidgwick, *loc. cit.*, p. 107.

intense. The entire host of organic compounds characterised by covalent linkages show the effect without any exception. These facts are essentially in agreement with the view put forward in this paper that the strength of the covalent linkage between the atoms decides the presence or absence of the Raman lines. The difference between two chlorides of the same metal, *viz.*, $SnCl_2$ and $SnCl_4$, the former a good conductor in the molten state and the later a non-conductor is shown by the absence of Raman lines in the one and by their presence in the other.

Apart from the conductivity in the molten state, conductivity in aqueous solutions, wherever it is possible, will give us an idea of the strength of the covalency bonds. The case of $HgCl_2$ as mentioned before illustrates this point. Progressive ionisation should result in a weakening of the Raman lines, as has indeed been found by Daure with solutions of antimony and bismuth chlorides.

Crystal structure.—As has already been pointed out, the broad division between ionic and molecular lattices finds a counterpart in the Raman spectra, the typical ionic crystals (NaCl, KCl) giving no lines while the typical molecular substances (CCl_4, Hg_2Cl_2) show prominent Raman lines. Substances belonging to the NaCl, CsCl and CaF_2 types are not favourable while the Hg_2Cl_2 (molecular) type is very favourable for the production of Raman lines, the CdI_2 type (Schichtengitter) being probably the transition stage.

Other Physical Properties.—Chief among these are volatility, power of forming stable organic derivatives and solubility in polar or non-polar solvents which serve to distinguish the electrovalent from the covalent type of linkage. The latter type of compounds as also those which show strong Raman spectra usually possess low melting and boiling points while the others like the alkali halides possess very low volatility. While the latter are freely soluble in water and almost insoluble in benzene, the former compounds dissolve in benzene

or other non-hydroxylic solvents with fair readiness. As Sidgwick points out,[20] however, the solubility and volatility may also be lessened by other causes such as polymerisation or association. Typical instances of this kind are the 'giant molecules' of diamond or silicon carbide, in which the whole crystal is one great molecule with all its atoms held together by covalent links. They possess no vapour pressure or solubility, and their melting and boiling points are very high. Their non-polar character could be judged only from their crystal structure.

The formation of alkyl or aryl derivatives is very characteristic of certain metals. Of these mercury is very prominent, and as Sidgwick says,[21] "Far more organic compounds are known of mercury than of all the other metals together." Lead and tin in the tetravalent condition, cadmium, germanium, zinc, boron, silicon, phosphorus, arsenic, antimony and bismuth form organic derivatives with great ease, *e.g.*, the alkyls, most of which are stable and possess low boiling points. There is no doubt that in these compounds covalent bonds are present. It is interesting to note that compounds of divalent lead and tin are comparatively rare. The presence of covalent bonds and the existence of Raman lines in the halides seem to go hand in hand with the power of forming stable organic compounds.

Raman Effect and the Periodic System.—Since only the valency electrons seem to be primarily concerned in the Raman effect, a consideration of the position occupied by the particular element in the periodic table would be of interest. The nature of the binding between the atoms in the halides from the point of view of their physical properties, *viz.*, their volatility, type of crystal lattice and electrical conductivity has been examined by Grimm and Sommerfeld, Goldschmidt

[20], [21] Sidgwick, *loc. cit.*, p. 89 and 264.

and by Bitz and Klemm. The following classification from a paper by Grimm [23] shows the division between the two types of halides:

TABLE V.

Fluorides.				Chlorides.			
LiF	BeF_2	*BF_3*	*CF_4*	LiCl	*$BeCl_2$*	*BCl_3*	*CCl_4*
NaF	MgF_2	AlF_3	*SiF_4*	NaCl	$MgCl_2$	*$AlCl_3$*	*$SiCl_4$*
KF	CaF_2	ScF_3	*TiF_4*	KCl	$CaCl_2$	$ScCl_3$	*$TiCl_4$*
RbF	SrF_2	YF_3	ZrF_4	RbCl	$SrCl_2$	YCl_3	$ZrCl_4$
CsF	BaF_2	LaF_3	CeF_4	CsCl	$BaCl_2$	$LaCl_3$	$CeCl_4$

Substances in italics are of the covalent type. The others are mostly of the electrovalent type.

The conclusion is arrived at that with increasing deforming effect of the cation (with decreasing radius and increasing charge) and also with increasing deformability of the anions (with increasing charge and size), the greater is the possibility of the transformation from the polar to the non-polar type, or, in other words, conversion of the electrovalent into covalent bonds. Hence the Raman effect should show a similar change, and at least among the halides this seems to be supported by the present experiments.

5. *Conclusion.*

It will be seen from the foregoing that the study of Raman spectra of crystals enables us to distinguish easily between the electrovalent and covalent types of linkages in chemical compounds. It gives valuable information about

[23] Grimm, Naturwiss., *17*, 538 (1929).

the shape and structure of the molecules in the crystal lattice in agreement with X-ray data. The calculation of the specific heats in the simpler crystals which show the effect is at present being attempted. Further work on the effect of solution and fusion on the Raman spectra of polar and non-polar inorganic and organic compounds is in progress which will throw considerable light on molecular association, rotational-vibrational effects in liquids and related questions.

I have great pleasure in thanking Prof. Sir C. V. Raman under whose inspiring guidance this work was carried out, for numerous suggestions and advice during its progress.

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